

Highly active Cu-ZnO catalysts for the WGS reaction at medium-high space velocities: effect of the support composition

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Abstract

Cu-ZnO based catalysts are the benchmark materials for the low-temperature WGS reaction. However, they present a crucial drawback which limits their application in portable devices: they only work under very low space velocities. In this study, we have developed a series of multicomponent Cu-ZnO catalysts able to work at relatively high space velocities with outstanding activity and stability. Different reference supports have been utilised with CeO₂-Al₂O₃ being the most promising system. Overall, this work describes a strategy to design advanced Cu-based catalysts that can overcome the residence time restrictions in the WGS reaction.

Keywords: Cu catalysts, space velocity, hydrogen fuel processors, WGS, cerium oxide.

1. Introduction

Hydrogen powered fuel cells are meant to play a pivotal role in the new global energy paradigm which pursues a shift towards low-carbon technologies. Hydrogen is typically produced from reforming reactions with the unavoidable generation of carbon monoxide, which is a harmful gas for the anode of the polymer electrolyte membrane fuel cells (PEM-FC). Therefore, the production of hydrogen pure enough to feed a PEM-FC involves a series of fuel processing reactions including hydrocarbon or biomass reforming, water-gas shift (WGS) reaction, preferential CO-oxidation and/or methanation. Among these processes the

WGS is the most crucial unit for H₂ clean up since it faces the highest amount of CO. The commercial catalysts for the water-gas shift reaction at low temperatures are mixtures of Cu and ZnO supported on alumina [1-15]. This formulation has remained almost unchangeable in the past decades. Indeed, despite its drawbacks (i.e. they are pyrophoric and they require previous activation) copper-based catalysts provide better activity/cost balance than noble metal-based systems such as Pt and Au, which have been intensively applied in this reaction [4-13].

The copper-based catalyst is an excellent formulation for static applications, but the implementation of the WGS units in fuel processors for portable applications imposes a limit in the reactor volume. This is the “Achilles heel” of the Cu-ZnO/Al₂O₃ catalysts, which for practical reasons are utilised in pellets to provide enough mass to avoid poisoning and increase the lifespan of the catalysts, thus resulting in very low space velocities (e.g. 2000-4000 h⁻¹) and making necessary big reactor volumes [2]. In response to this need, this work aims to develop high performance Cu-ZnO catalysts able to operate at medium-high space velocities in order to overcome the volume restrictions that limit the application of these cost-effective materials in portable devices. Also, given the well documented importance of the support in the shift reaction [14-21], four reference supports have been selected in this paper to determine their effect on the WGS activity when working beyond the typical low space velocity range.

2. Experimental

2.1 Catalyst preparation

Experimental details on catalysts preparation are reported in the Supporting Info. Briefly, the samples are composed of 15 wt.% CuO and 5 wt.% ZnO finely dispersed on the support (Al₂O₃ – Sasol; CeO₂-Al₂O₃ – Puralox, Sasol; SiO₂ - CARiACT Q-6 and ZSM-5 ammonium, 23:1 mol SiO₂:Al₂O₃ – AlfaAesar). The variety of supports provides a complete picture of the carrier influence. In fact, they have been intentionally selected given their disparity in terms of textural properties (see Table S1 supporting info), redox behaviour and acid/base features.

2.2 Characterization

The physicochemical characterisation of the samples was determined by X-Ray diffraction (XRD), temperature-programed reduction (TPR) experiments and Raman spectroscopy. (see Supporting Information for more details).

2.3 Catalytic activity and selectivity

The catalytic conditions, calculations and a detailed description of the equipment can be found in the Supporting Information.

3. Results and discussion

Figure 1 shows the catalytic screening in the WGS reaction of the prepared catalysts in a model WGS mixture at 9000 h^{-1} (more than four times the space velocity in industrial stationary applications $\sim 2000\text{ h}^{-1}$). The plot clearly reveals the effect of the support in the catalytic activity. While the catalysts supported on SiO_2 and ZSM-5 zeolite are not able to fully abate CO, the solids supported on Al_2O_3 and $\text{CeO}_2\text{-Al}_2\text{O}_3$ reach full conversion at 300 and 225°C respectively. This is an excellent result especially when compared with the commercial catalyst's activity (adapted from ref [22]) and tested at much lower space velocity. Indeed, the harsh residence time utilised in the catalytic tests highlights the importance of the achieved results. Even more remarkable is the extraordinary CO conversion levels reached by the Cu-ZnO/ $\text{CeO}_2\text{-Al}_2\text{O}_3$ sample, with total CO conversion at rather low temperature. Yet, this catalyst outperforms the activity of Cu-based systems promoted with Au and measured at lower spaces velocities as those recently reported elsewhere [21].

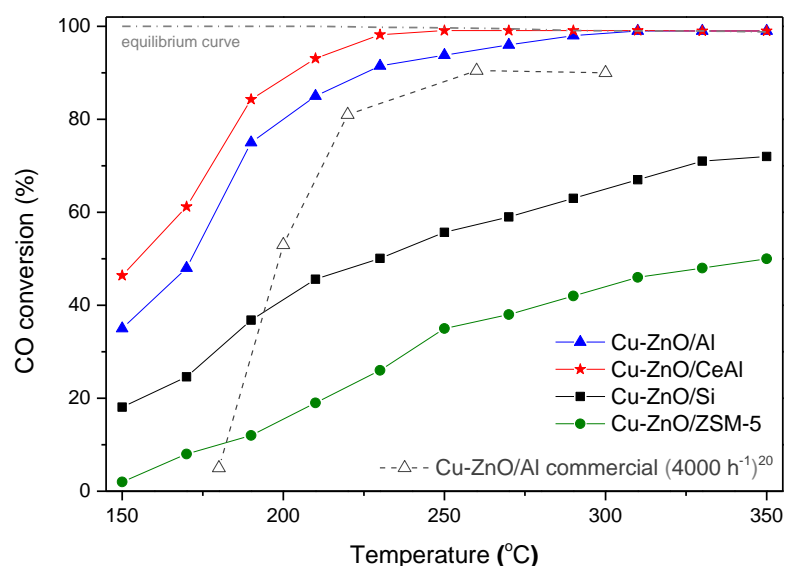


Figure 1. Catalytic activity in a model WGS mixture (4.5% CO, 30% H₂O in He at 9000 h⁻¹).

In order to establish a more general comparison with previously reported highly active shift catalysts, the reaction rates at 180 °C were calculated and presented in **Table 1**. As shown in the table, the Cu-ZnO/CeO₂-Al₂O₃ and Cu-ZnO/Al₂O₃ catalysts are much better systems than the reference commercial CuO-ZnO catalyst reported in literature. Furthermore, our catalysts are clearly superior to noble metal-based catalysts tested at much lower space velocities, what reinforces the exceptional behaviour of the developed system.

Table 1. WGS reaction rates at 180 °C normalised per mol of active phase (Cu, Au and Pt were considered as active phases)

¹: Data obtained from Figure 2 (post reforming WGS conditions)

For a practical application in hydrogen clean-up goals, the most active catalysts were tested under a realistic WGS mixture (including CO₂ and H₂). The results (**Figure 2**) reveal that despite the expected shift of the conversion curve towards higher temperature (as a direct consequence of Le Chatelier principle) the Cu-ZnO/CeO₂-Al₂O₃ catalyst presents elevated CO conversion levels and showing much better conversion than the Cu-ZnO/Al₂O₃ sample. For further comparison, catalytic data of commercial samples tested in fairly similar reaction mixtures available in literature have been included in Figure 2. For example in the paper by Mendes and co-workers [25], they studied a commercial catalyst (green line) which is more active than our homemade systems (blue lines in the Figure 2). However, this catalyst was tested at much lower space velocity than ours. On the other hand, Pingjun et al. [26] prepared a commercial-like copper catalyst able to work at rather high space velocity (red line) with

| Sample | WGS rates (mol CO converted/s* mol active phase x 10 ⁴) | GHSV (h ⁻¹) | WHSV (mLg ⁻¹ h ⁻¹) |
|--|--|-------------------------|---|
| Cu-ZnO/Al ₂ O ₃ | 20.4 | 9000 | 12000 |
| Cu-ZnO/CeO ₂ -Al ₂ O ₃ | 26.5 | 9000 | 12000 |
| Cu-ZnO/SiO ₂ | 10.9 | 9000 | 12000 |
| Cu-ZnO/ZSM-5 | 3.5 | 9000 | 12000 |
| commercial CuO-ZnO/Al ₂ O ₃ [22] | 0.8 | 4000 | - |
| CuCe _{0.95} Zn _{0.05} [22] | 21.7 | 4000 | - |
| Au/CeO ₂ -CuO [21] | 1.3 | 4000 | 6000 |
| Pt/Al ₂ O ₃ [23] | 5.1 | 4000 | 6000 |
| Cu-ZnO/Al ₂ O ₃ hydrotalcite [24] | 0.2 | 4000 | 6000 |
| Au/Cu-ZnO/Al ₂ O ₃ hydrotalcite [24] | 6.3 | 4000 | 6000 |
| ¹ Cu-ZnO/CeO ₂ -Al ₂ O ₃ | 10.3 | 9000 | 12000 |
| ¹ commercial 50% Cu-40% ZnO/Al ₂ O ₃ [25] | 9.2 | - | 4800 |
| ¹ commercial 42% Cu-ZnO/Al ₂ O ₃ [26] | 4.9 | 30000 | - |

elevated conversions at low temperature. These two commercial systems seem to

outperform the activity of our catalysts. Nevertheless, the main advantage of our catalysts must be mentioned at this point, and this is the very low Cu loading compared to the typical commercial systems (i.e. the catalysts in this study present 15 wt.% Cu while the commercial catalysts are in the 40-50 wt.% range of Cu). The balance low copper loading/high performance highlights the potential impact of our catalysts in the WGS reaction. Indeed, if the apparent reaction rates are calculated (Table 1) the superiority of our catalysts becomes clearer.

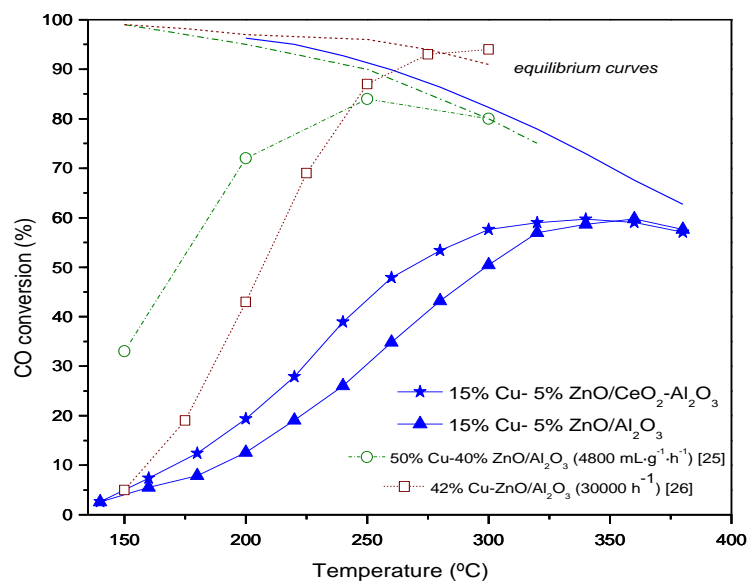


Figure 2. Catalytic activity comparison of our samples (25% H₂O + 8% CO + 37% H₂ + 8% CO₂), a 50%Cu-40%ZnO/Al₂O₃ commercial sample (16.90% H₂O + 4.75% CO + 28.46% H₂ + 10.06% CO₂) [25] and a commercial-like 42%Cu-ZnO/Al₂O₃ sample (27% H₂O + 11% CO + 26% H₂ + 7% CO₂) [26] in a post-reforming WGS mixture.

Furthermore, this catalyst displayed great stability showing just small activity depletion (from 38% to 31% CO conversion) after working for more than 160 hours of continuous operation under realistic conditions (**Figure 3**). In addition, when portable applications are targeted, the catalysts in the WGS unit must withstand eventual start-up/shutdowns situations [26, 27]. This kind of stability experiments are the most demanding tests for a WGS catalyst since during the cooling down, liquid water may condensate on the pores of the catalysts causing severe deactivation. However, as pictured in **Figure 3**, our Cu-Zn/CeO₂-Al₂O₃ catalyst is rather robust towards start/stop cycles. The first contact with liquid water dropped the CO conversion to 24% but after 4 cycles the conversion was stabilised at 20% (it should be mentioned that the cycles were conducted right after the long term stability test). A similar test was carried out for the 42%Cu-Zn/Al₂O₃ catalysts in ref [26]. Herein, they observed that

after only 7 hours of stability test and 4 start/stop cycles the conversion drops drastically to 20%. In contrast, we run our stability during 160 h (long term test) plus 12 hours of start/stop cycles showing better results than those exhibited by the commercial catalysts. The later, emphasises the suitability of this catalyst for direct application in integrated reforming-WGS fuel processors. Indeed, as stated by Farrauto et al. the commercial CuZn WGS catalyst suffers for irreversible loss of activity upon exposure to liquid water during start-up and shut-down cycles and cannot be regenerated [28]. Indeed, partial oxidation of copper and/or sintering of the metallic phase could happen. However, the post reaction XRD (Figure S2 and Table S2 supporting info) reveals that Cu remains as metallic after the standard runs and also after the stability tests. Furthermore, sintering does not seem to be important for these catalysts. A slight increase in the Cu particle size was detected for the Cu-Zn/ Al_2O_3 while the Cu-ZnO/ CeO_2 - Al_2O_3 maintains its copper particle size almost constant even after the stability tests. The later reveals the role of ceria: it not only promotes the catalytic activity but also improves the stability.

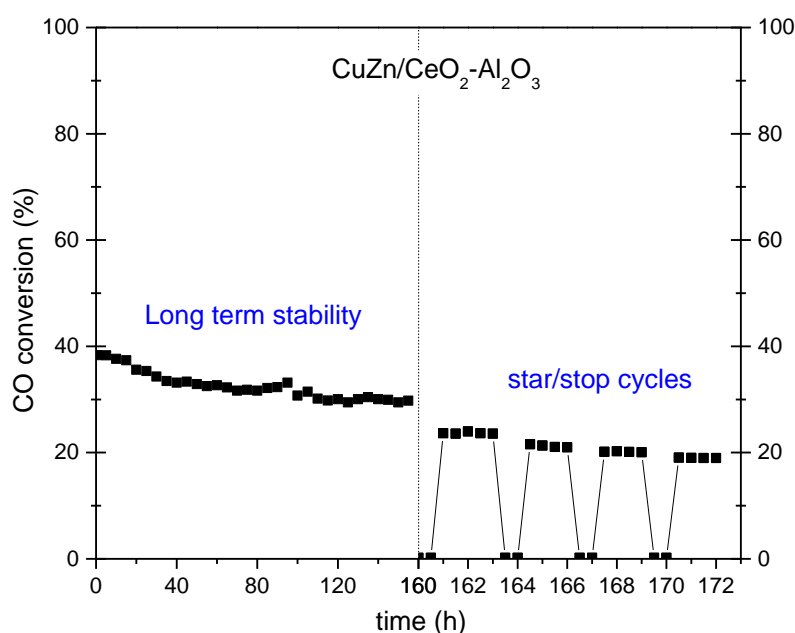


Figure 3. Long-term stability test and start-up/shutdowns study at 250 °C and post-reforming WGS mixture at 9000 h⁻¹

The physicochemical characterisation provides some clues to explain the superior activity of the Cu-ZnO/ CeO_2 - Al_2O_3 catalyst over the other systems included in this study. The XRD patterns (Figure S1 supporting info) indicate the presence of crystalline CuO species after calcination. Some peaks related to the different supports have been detected (e.g. diffraction

lines of CeO₂ fluorite cubic cell for the CeO₂-Al₂O₃ support and zeolite peaks for the system supported on ZSM-5). No diffraction signals related to ZnO were found, pointing a good dispersion of this oxide in all the samples. As for the Raman analysis (Figure S2, supporting info) all the samples presented the main Raman modes of cupric oxide (A_{1g} + 2B_g) at 275 cm⁻¹, 330 cm⁻¹ and 619 cm⁻¹ as described by Xu et al [29]. Herein, the ceria based sample present an additional Raman mode at 442 cm⁻¹ which can be attributed to the symmetric breathing mode, F_{2g}, of the oxygen atoms surrounding the Ce⁴⁺ ions in the fluorite structure [30]. The presence of ceria in close contact with CuO results in electronic perturbations and creation of surface defects in both oxides, making the CuO/CeO₂ interface an ideal reactive site for CO and H₂O in the shift reaction, as reported elsewhere [21]. Indeed, the band at 560 cm⁻¹ observed in this sample is associated to oxygen vacancies – Ov – confirming the presence of oxygen defects in ceria.

The redox properties of the catalysts were studied by means of H₂-TPR, and the results are presented in **Figure 4**. The simplest profile was obtained for the Cu-ZnO/Al₂O₃ sample, which only presented one reduction zone centred at 268 °C associated to the reduction of CuO to metallic Cu, as previously indicated by Shishido et al. [31]. The catalysts supported on SiO₂ and ZSM-5 presented two reduction zones, indicating the presence of different types of CuO particles and CuO-support interactions. As for the Cu-ZnO/CeO₂-Al₂O₃ catalyst, two reduction zones with a shoulder in the second one were found. This profile accounts for the reduction of CuO and probably the simultaneous reduction of CeO₂ surface species [21]. The parallel reduction of CuO and CeO₂ indicates an intimate Cu-CeO₂ contact, in fair agreement with the Raman results. Indeed, according to the TPR profile, the pre-reduction treatment before every catalytic run results in full reduction of Cu and partial reduction of CeO₂, thus leading to a Cu-ZnO/CeO_{2-x} system supported on alumina. This configuration is key to understand the exceptional behaviour of this catalyst. As stated by Rodriguez's group, Cu/CeO_{2-x} (and the inverse CeO_{2-x}/Cu) are excellent catalysts for the shift reaction where the oxygen vacancies on ceria play a critical role for water activation (the rate limiting step) [18, 32]. Furthermore, the oxygen mobility of ceria linked to its extensive oxygen storage capacity converts cerium oxide in the ideal promoter for a redox reaction such as the WGS [21]. On the other hand, Cu-ZnO/Al₂O₃ is a benchmark catalyst for this reaction. As a result, the outstanding performance of our multicomponent Cu-ZnO/CeO₂-Al₂O₃ catalyst is just the careful combination of the excellent skills of Cu-ZnO/Al₂O₃ plus the redox promotion introduced by

ceria. The later also eases the reaction barrier via water activation on its oxygen vacancies, which formation is favoured due to the intimate CuO-CeO₂ interaction.

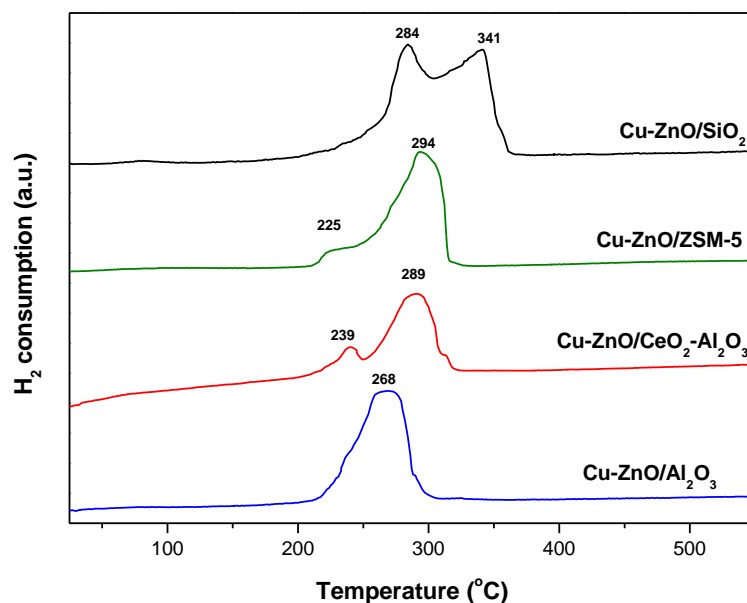


Figure 4. H₂-TPR profiles.

4. Conclusions

The redox and structural promotion described above has been successfully incorporated in this paper to jump the space velocity limitations of the Cu based catalysts in the shift reaction. Somehow our results connect the physical chemistry knowledge in CeO₂ promoted Cu catalysts with the engineering needs of hydrogen fuel processors.

Overall, the developed Cu based catalysts are able to work successfully at relatively high spaces velocities in close to real conditions for portable applications. This kind of catalysts outperforms the catalytic activity of state of the art materials reported so far, some of them based on noble metals. Yet more, the excellent catalytic behaviour displayed by our Cu-ZnO/CeO₂-Al₂O₃ catalyst is reinforced by its high stability and tolerance to start/stop situations which seems to be associated to the presence of ceria avoiding copper oxidation and sintering. Currently, further investigations are on-going in our labs to expand the evidences in the observed performance. In any case, the design strategy presented herein opens new avenues for research in cost-effective and highly performing catalysts for the hydrogen economy.

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